ON THE RAMAN SPECTRA OF 1, 2-DICHLOROETHANE AND 1, 1, 2-TRICHLOROETHANE IN THE VAPOUR STATE*

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Plate XVII

ABSTRACT. The ratio of intensities of the lines 755 and 654 cm^{-1} in the Raman spectrum of 1, 2-dichloroethane vapour at 135°C has been measured quantitatively and compared with that reported for the vapour at 170°C by previous workers. It has been observed that a catastrophic change in the intensity ratio takes place with the change of state from liquid to vapour phase. The values of the intensity ratio, however, change only very slightly with the change of temperature of the vapour from 135°C to 170°C, so that the difference in energies of the two types of molecules to which the two lines are attributed remains the same in the case of the vapour as in the case of the liquid. It is pointed out that the catastrophic change in the intensity ratio cannot be explained on the assumption that two types of molecules co-exist in the liquid, the relative populations of the molecules depending on their partition functions and energy difference, and that some sort of stronger interaction between the molecules in the liquid state is to be postulated to explain the apparently anomalous results.

In the case of 1, 1, 2-trichloroethane the line 775 cm^{-1} for the liquid at 120°C is totally absent in the spectrum due to the vapour at 170°C. It is pointed out that this change takes place with the change from liquid to the vapour state., Probable explanation for this phenomenon has been offered.

INTRODUCTION

The Raman spectra of 1,2- dichloroethane in the liquid and solid phases have been investigated previously by Mizushima *et al* (1938) and Bishui (1948). It was observed that some of the prominent Raman lines disappear when the liquid is solidified. Mizushima *et al* (1938) pointed out that the Raman spectrum of the substance in the solid state can be explained on the assumption that the molecules are of the trans form in the solid state while the Raman lines due to the liquid phase are probably due to two types of molecules, one of the 'trans' configuration and the other of the 'gauche' configuration. They also studied the Raman spectrum of the substance in the vapour state at 170°C (Mizushima *et al*, 1949) and observed that the spectrum corresponds to that due to a mixture of trans and gauche molecules in the ratio 1 : 0.34, while in the liquid state the ratio was found

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to be 1 : 1.3. In the solid state the gauche molecules are found to be totally absent and all the molecules are of the trans type (Mizushima *et al*, 1938). It is thus evident that if the ratio of the two types of the molecules depended on temperature alone the proportion of molecules of the gauche type should have been larger in the case of the vapour at 170°C than that in the case of the liquid at room temperature. Actually, however, the proportion diminishes with increase of temperature. This behaviour is thus anomalous. The object of the present investigation was to find out whether at a temperature lower than 170°C the ratio of the intensities of the two lines 768 and 666 cm^{-1}, assumed to be due to the trans and gauche molecules respectively in the vapour phase, is the same as or different from that observed in the case of the vapour at 170°C. It was also thought worthwhile to investigate whether any other substituted ethane behaves in the same way with the change from liquid to vapour phase as 1,2-dichloroethane. For this purpose the Raman spectrum of 1, 1, 2-trichloroethane in the vapour state at 170°C has been investigated and the results have been discussed in the present paper.

EXPERIMENTAL

A Pyrex tube about 6 cm in diameter and 38 cm long was used as the Wood's tube. Requisite quantity of the distilled liquid was introduced in the tube and it was sealed at the tail end after evacuation. The tube was placed in a horizontal cylindrical electric heater provided with two long windows parallel to its axis. The temperature of the vapour was raised to about 135°C and 170°C in the case of 1,2-dichloroethane and 1,1,2-trichloroethane respectively and the vapour filled the tube at pressure of about four atmospheres in both the cases. The temperatures were measured with a mercury thermometer inserted in the heater with tube inserted in it and two mercury arcs running in their positions. There was an excess of liquid in the tube, about 1 c.c. in volume, and this was contained in a blackened bulb at the tail end of the tube. The bulb was connected to the tube through a bent tube so that this liquid was not visible through the window of the Wood's tube. Two long mercury arcs of Pyrex glass made in the laboratory were placed near and parallel to the two windows of the heater and they were focussed on to the Wood's tube with two cylindrical mirrors made of polished aluminium sheets.

An Adam Hilger two-prism glass spectrograph was used to photograph the Raman spectra. The dispersion was about 21 Å per mm. in the 4046 Å region. An exposure of about 100 hours was necessary to record the Raman lines due to the vapour with moderate densities. Ilford Zenith plates taken from a fresh packet were used. Suitable stops were used to prevent extraneous light from entering into the spectrograph. In the case of 1, 2-dichloroethane vapour a strip of black paper was placed in the position of the 4358 Å line to cut off this line, so that due to over exposure the line

might not produce blackening in its neighbourhood on the photographic plate.

In order to measure the relative intensities of the lines 668 and 762 cm^{-1} of 1,2-dichloroethane intensity marks were taken on a plate taken from the same packet using light from a tungsten filament bulb reflected from a strip of white unglazed paper and by varying the width of the slit of the spectrograph. The plates containing the Raman spectrum and that containing the intensity marks were developed under identical conditions. Microphotometric records of the lines were taken with a Kipp and Zonen type self-recording microphotometer. The relative intensities of the two Raman lines were found out from the densities of the lines with the help of the blackening log-intensity curves for the two wavelengths corresponding to these two lines drawn with the help of the intensity marks. The background intensities were deducted from the total intensities at the centres of the lines in order to find out the relative intensities of the lines alone. In both cases Raman spectra of the liquids at room temperature and at temperatures slightly below the temperatures of the vapour were also photographed. As the line 654 cm^{-1} is narrower than the line 755 cm^{-1} in the case of the liquid as well as the vapour phase the intensities were multiplied by the relative widths of the lines to get the integrated intensities.

RESULTS AND DISCUSSION

The Raman spectra of 1,2-dichloroethane in the vapour state at 135°C and in the liquid state at 30°C and 130°C are reproduced in the Plate XVII, figures 1(*a*), 1(*b*) and 1(*c*). The spectra for 1,1,2-trichloroethane in the vapour state at 170°C and in the liquid state at 30°C and 120°C respectively, are reproduced in figures 2(*a*), 2(*b*) and 2(*c*) in Plate XVII. The frequency-shifts are given in Tables I and II respectively. Microphotometric records of the lines due to 1,2-dichloroethane having frequency-shifts in the range 500-1000 cm^{-1} are reproduced in figure 3.

It can be seen from Table I that when 1, 2-dichloroethane in liquid phase is heated to 130°C its Raman spectrum does not change appreciably. The Raman spectrum, however, undergoes considerable changes with the change from liquid to vapour phase. The lines 755, 680 and 658 cm^{-1} due to the liquid at 130°C shift respectively to 762, 702 and 668 cm^{-1} in the case of the vapour at 135°C. Also the lines 2958 and 3005 cm^{-1} due to C-H valence oscillation, shift respectively to 2972 and 3024 cm^{-1} with the change of state mentioned above. As regards the ratio of the intensity of the line 755 cm^{-1} to that of the line 654 cm^{-1} quantitative measurement by spectrophotometric method gave the results given in Table III, in which the data reported by Morino *et al* (1941) are also reported.

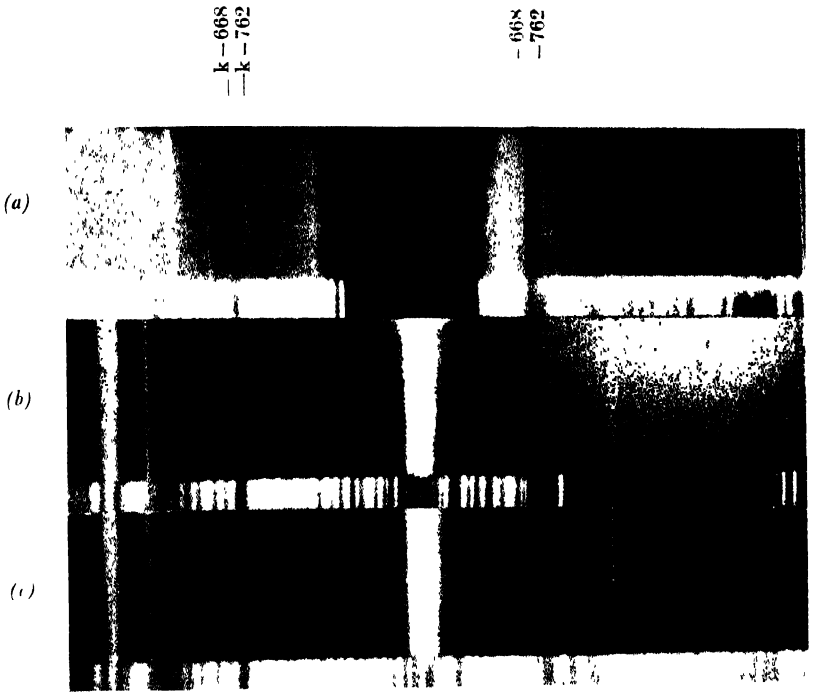

Fig. 1

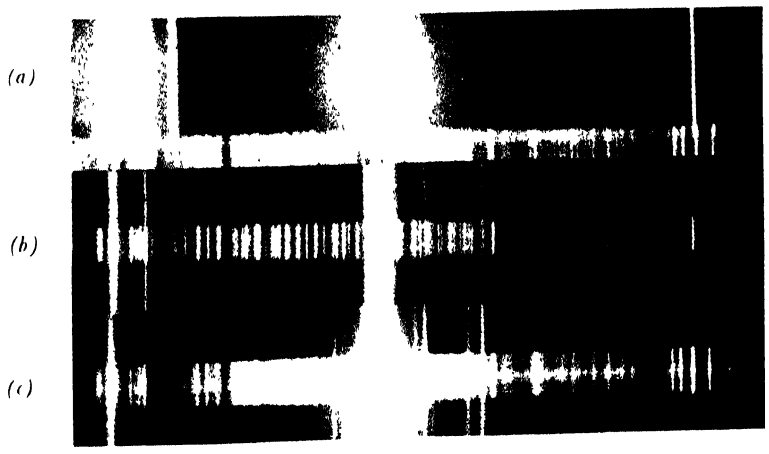

Fig. 2
Raman spectra

Fig. 1. 1, 2-Dichloroethane
(a) Vapour at 135°C
(b) Liquid at 130°C
(c) „ „ 30°C

Fig. 2. 1, 1, 2-Trichloroethane
(a) Vapour at 170°C
(b) Liquid at 120°C
(c) „ „ 30°C

TABLE I

1, 2-Dichloroethane, $ClCH_2{\cdot}CH_2Cl$.

$\Delta\nu$ in cm^{-1}

Liquid state		Vapour state.	
at 30 C°	at about 130 °C	at about 135°C	at about 170°C, Mizushima *et. al* (1949)
128 (3b) e, k	128 (1) e, k		
265 (1) e	265 (1) e		
300 (6) e, k	30 (3) e, k	30 (3) e k	301 (7)
409 (2) e, k	409 (1b)		
654 (8) e, k	658 (3) e k	668 (1) e, k	660 (1)
676 (3) e, k	680 (0) e, k	702 (1) e, k	689 (0)
755 (10) e, k	7-5 (6) e, k	762 (4) e, k	768 (10)
833 (0) e, k	833 (0) e, k		950 (?)
946 (1) e, k	946 (1) e, k		
1051 (0) e, k	1051 (1) e, k		1040 (?)
1150 (0) k	1150 (0) k		
1250 (2) k	1250 (1) k		
1298 (3) e, k	1298 (2) e, k	1300 (1) e, k	1305 (3)
1430 (2) e, k	1430 (1) e, k		
1443 (2) e, k	1443 (1) e, k		
2880 (0) e, k	2880 (0) e, k	2880 (0) e, k	2887 (1) ?
2958 (8) k	2958 (6) k	2972 (3) e, k	2972 (8)
3005 (4b) e, k	3005 (2) e, k	3024 (1b) e, k	2978 (8)

TABLE II

1, 1, 2-Trichloroethane, $CHCl_2CH_2Cl$

$\Delta\nu$ in cm^{-1}

Solid state at -180°C Biswas (1953).	Liquid state. at 30°C.	Liquid state. at about 120°C.	Vapour state at about 170° C.
60 (1) e	118 (2b) e, k	118 (1) e, k	
125 (0) e			
156 (1) e	190 (1b) e	190 (0) e	
263 (2) e, k	258 (4) e, k	258 (3) e, k	
290 (0) e	287 (2) e, k	287 (1) e, k	
338 (3) e, k	333 (10) e, k	333 (6) e, k	333 (2) e, k
385 (0) e	390 (4) e, k	390 (2) e, k	
525 (1)e	525 (2) e, k	526 (1) e, k	
	638 (4) e, k	638 (2) e, k	
670 (3) e, k	668 (6) e, k	668 (3) e, k	668 (1b) e, k
	697 (0) e	697 (0) e	
	727 (0) e	727 (0) e	
772 (6) e, k	775 (8) e, k	775 (6) e, k	
	786 (5) e, k	786 (6) e, k	793 (4) e, k
934 (0) e ?	934 (2) e	934 (1) e	
	1041 (1) e, k	1041 (0) e, k	
1260 (0) e	1260 (2) e, k	1260 (1) e, k	
1304 (0) e	1304 (3) e k	1304 (1) e, k	
1427 (1) e	1430 (3) e, k	1430 (1) e, k	
2961 (4) e, k	2961 (4) e, k	2962 (2) k	2976 (3) k
3005 (3) e, k	3001 (2) e, k	3002 (1) e, k	3001 (1) e, k

TABLE III

Intensity ratio I_{755}/I_{654}/(k-excitation)

Present author.			Morino *et al* (1941).		
Liquid at 30°C.	Liquid at 130°C.	Vapour at 135°C.	Liquid at 25°C.	Liquid at 150°C.	Vapour at 170°C.
1.8 : 1	2.0 : 1	4.5 : 1	1.9 : 1	2.1 : 1	5 : 1

It is thus evident that the line 755 cm^{-1} not only shifts to 762 and 768 cm^{-1} with vaporization and increase of temperature to 130°C and 170°C respectively, but also the ratio of the intensities of the two lines 755 cm^{-1} and 654 cm^{-1} increases with the change of state. Further, this ratio is found to be 4.5 : 1 in the case of the vapour at 130°C, while Morino *et al* (1941) found that in the case of the vapour at 170°C the ratio is 5 : 1. Hence the ratio changes only slightly with the rise of temperature of the vapour. There are some discrepancies between the results reported by Mizushima *et al* (1949) for the vapour at 170°C and those obtained in the present investigation. First, in place of the two lines 2958 and 3005 cm^{-1} due to C-H valence oscillations of the 1, 2-dichloroethane in the liquid phase they observed two equally intense lines at 2962 and 2978 cm^{-1} in the case of the vapour at 170°C. In the present investigation a strong line at 2972 cm^{-1} and another faint line at 3024 cm^{-1} have been observed in the case of the vapour at 135°C. Probably the line 2972 cm^{-1} has been split up into components at 170°C, but at 135°C there is no indication of such a splitting or broadening of the line and the line 3024 cm^{-1} is definitely present in the spectrum due to vapour at 135°C. Secondly, the faint line 680 cm^{-1} due to the liquid at 130°C has been observed to shift to 689 cm^{-1} by the authors mentioned above and they have found the intensity of the line to be of the order zero in the vapour state although that of the line 666 cm^{-1} is 4. In the present investigation it is found that in the case of vapour at 135°C the line shifts to 702 cm^{-1} and its intensity is about half that of the line 668 cm^{-1}. This line can be clearly seen in the microphotometric records reproduced in figure 3.

The general conclusion drawn by Mizushima *et al* (1949) that the ratio of the intensity of the line 755 cm^{-1} and that of the line 654 cm^{-1} increases several times with vaporization of the liquid, is confirmed by the results of the present investigation. These results have been interpreted by the authors mentioned above on the assumption that the energy difference of the two types of molecules changes with the change from liquid to the vapour phase. Even if this assumption were correct, the shift and change in the relative intensity of the line 676 cm^{-1} with vaporisation of the liquid could not be

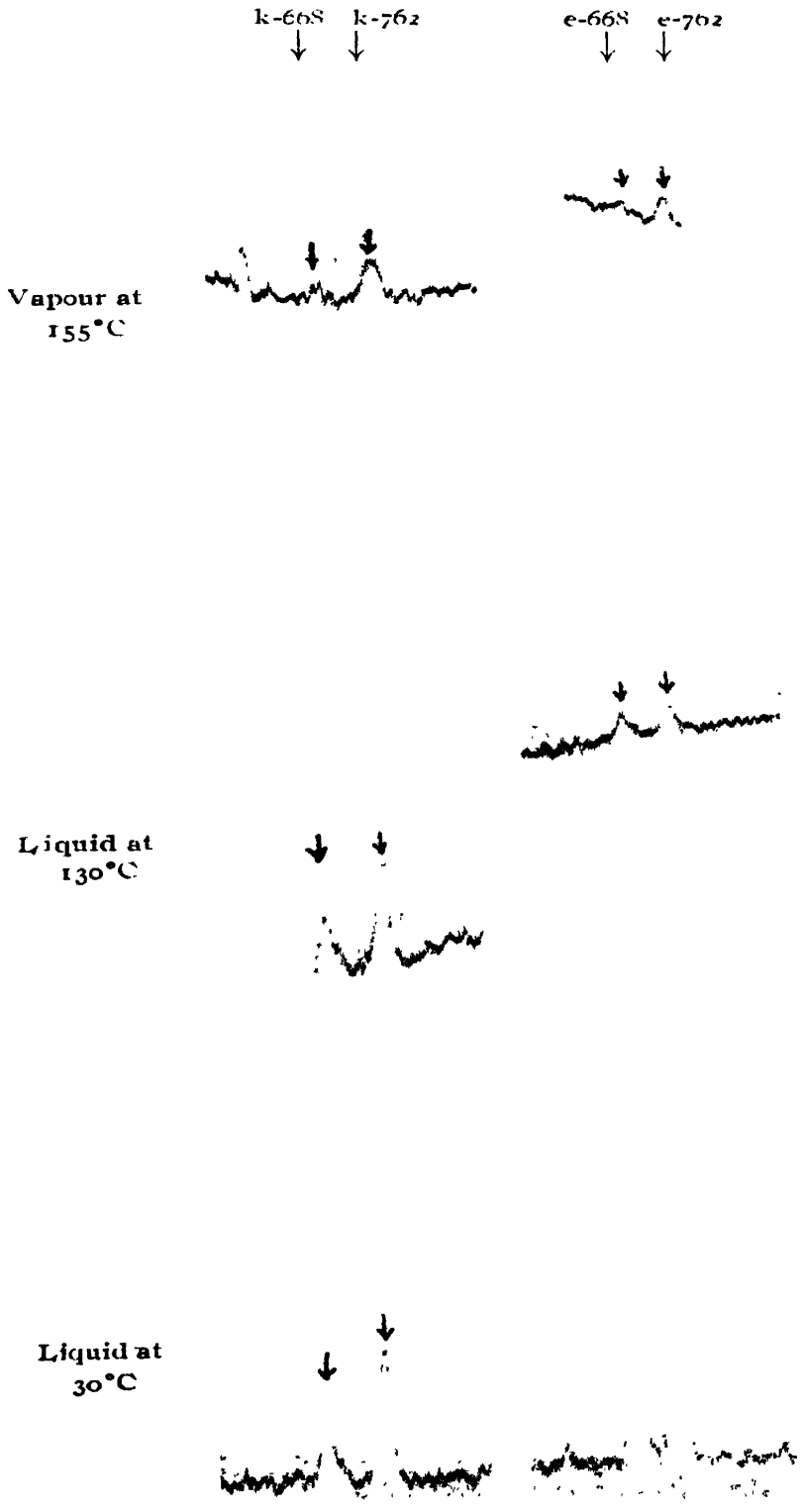
k-668
k-762
e-668
e-702
Vapour at 155°C
Liquid at 130°C
Liquid at 30°C

FIG. 3

explained on such a hypothesis. The results of the present investigation show that the ratio of the intensities of the lines 762 and 668 cm^{-1} due to the vapour at 135°C is 4.5:1, while the value of this ratio reported by Morino *et al* (1941) for the vapour at 170°C is 5:1. This fact clearly shows that if the two lines 655 cm^{-1} and 754 cm^{-1} are attributed to the gauche and trans configurations of the molecules respectively the difference in potential energies of the two types in the vapour state is almost the same as that observed in the case of the liquid. This fact is contradictory to the conclusion arrived at by Mizushima *et al* (1949) that the change in the intensity ratio of the two lines mentioned above is due to a change in the difference of energies of the two types of molecules with vaporisation of the liquid. The ratio of the intensities of the two lines according to their hypothesis would depend on the ratio of partition functions and the difference of energies of the two configurations. The partition function cannot change with the change of state, because the frequencies of vibration do not change appreciably with vaporization. Since the difference in energies of the two forms also remains unaltered with the change from liquid to vapour state, as observed in the present investigation, the catastrophic change in the ratio of intensities of the two lines which takes place with the change from liquid to vapour phase can not be explained by the hypothesis put forward by Mizushima *et al* (1949). An alternative explanation is, therefore, to be found out for this catastrophic change.

The change in the relative intensities of the lines 658 and 755 cm^{-1} with the change from liquid to vapour phase is, however, in the wrong direction, because it was observed by Mizushima *et al* (1938) that the line 658 cm^{-1} disappears with lowering of temperature and solidification of the liquid. If the change were due to energy difference of two types of molecules the intensity of the 658 cm^{-1} ought to have increased with increase of temperature of the liquid and the vapour. Actually, the reverse is true. The influence of the surrounding molecules in the liquid and solid states is thus mainly responsible for this anomalous behaviour of the molecule in these states of aggregation. Mizushima *et al* (1949) have stated that the presence of Onsäger field in the liquid is responsible for the change in the energy difference which is observed to take place with the changes from liquid to vapour phase. As pointed out earlier, no such change in the energy difference actually occurs with vaporisation and Onsäger field is not strong enough to produce the large change in the intensity ratio of the two lines mentioned above. Probably, some virtual bond is formed between neighbouring molecules in the liquid state so that the strength of one of the C-Cl bonds may be altered slightly. A satisfactory explanation of the observed changes in intensities of the two lines mentioned above cannot be given without collecting data for a few more molecules of the same type.

It would be interesting to find out whether 1,1,2-trichloroethane which is also a substituted ethane gives such anomalous results. Table II shows

that the intensity of the line 786 cm^{-1} due to liquid at 30°C increases slightly when the temperature of the liquid is raised to 120°C and that of the line 775 cm^{-1} diminishes a little. In the case of the vapour at 170°C, however, the latter line is totally absent and only a line at 793 cm^{-1} is observed. The width of the line at 793 cm^{-1} is much less than the total width of the doublet 775 and 786 cm^{-1} observed in the case of the liquid phase at 30°C. It was further observed by Biswas (1053) that the line 780 cm^{-} is totally absent in the Raman spectrum of the crystals of 1,1,2-trichloroethane at -180°C. Thus in this particular case the change in intensity of the line with change in state from solid to liquid phase and from liquid to vapour phase is in the same direction. These results can be interpreted by two alternative hypothesis. The lines 775 and 786 cm^{-1} may be due to either two different configurations of the molecule or one may be due to strongly associated molecules in the state of aggregation and the other due to single molecules. In the latter case the vapour state of the substance contains single molecules. The influence of intermolecular field in the liquid state may be responsible for both the change in configuration or formation of virtual bonds between some of the neighbouring molecules and in the solid state all the molecules may be transformed into one of the two types or the associated type. The disappearance of the line 775 cm^{-1} with vaporisation of the liquid is, however, not due to change of temperature of the molecule but it is due to change of state, because the line is as intense as the line 786 cm^{-1} even in the case of the liquid at 120°C. Thus in this case also the intermolecular field is responsible for the appearance of this line. It is difficult to understand why the influence of intermolecular field is necessary for the coexistence of two different configurations of the molecule. On the other hand, the appearance of the line 775 cm^{-1} only in the case of the liquid, may indicate that associated groups of molecules in the liquid are responsible for the origin of this line.

A comparison of the spectra of 1,2-dichloroethane and 1,1,2 trichloroethane in different states and at different temperatures thus shows that the behaviour of the former molecule is extremely anomalous and the hypothesis that two types of molecules coexist in the liquid and vapour phases cannot explain the observed facts satisfactorily.

Investigations with other similar compounds are in progress.

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